

# Lecture 12 – Oxygen deficiency in the geological record

- Biomarkers and paleoenvironments
  - Plankton ecology
  - Redox changes and water column stratification
  - Sea-surface temperature
- Mechanisms for ocean deoxygenation
- Examples of oceanic anoxic events (OAEs)
  - Cretaceous OAE-2 (Cenomanian-Turonian, ~93.5 Ma)
  - Permian-Triassic mass extinction (~252 Ma)

# Global marine primary production - sized

Microphytoplankton >20  $\mu\text{m}$   
Diatoms & Dinoflagellates

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Please see the images on  
[http://www.obs-vlfr.fr/LOV/OMT/fichiers\\_PDF/Uitz\\_et\\_al.\\_GBC\\_10.pdf](http://www.obs-vlfr.fr/LOV/OMT/fichiers_PDF/Uitz_et_al._GBC_10.pdf)

Nanophytoplankton 2-20  $\mu\text{m}$   
Prymnesiophytes

Picophytoplankton <2  $\mu\text{m}$   
Cyanobacteria

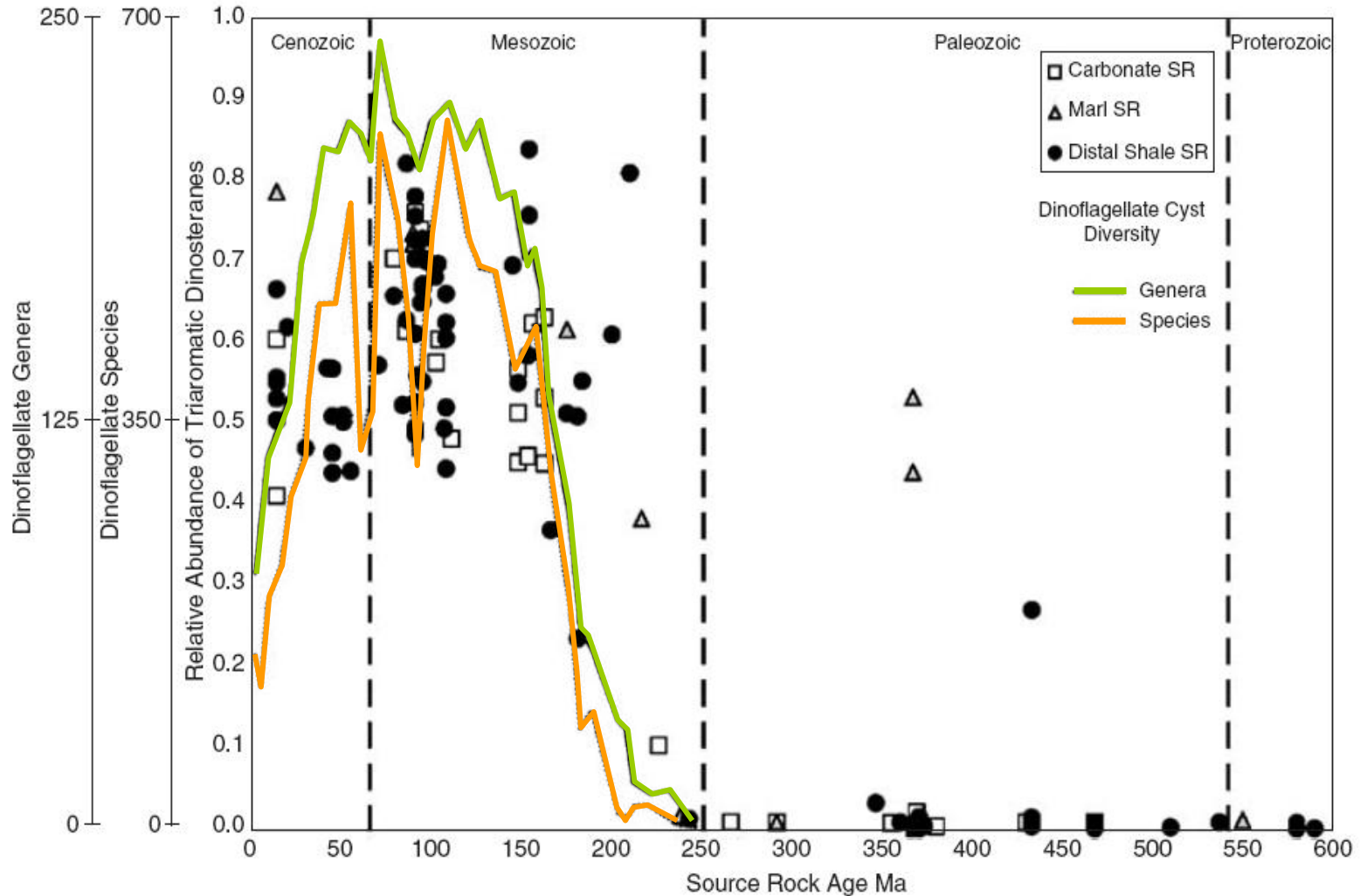
# Evolution of modern marine phytoplankton

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# Biomarkers & phytoplankton evolution

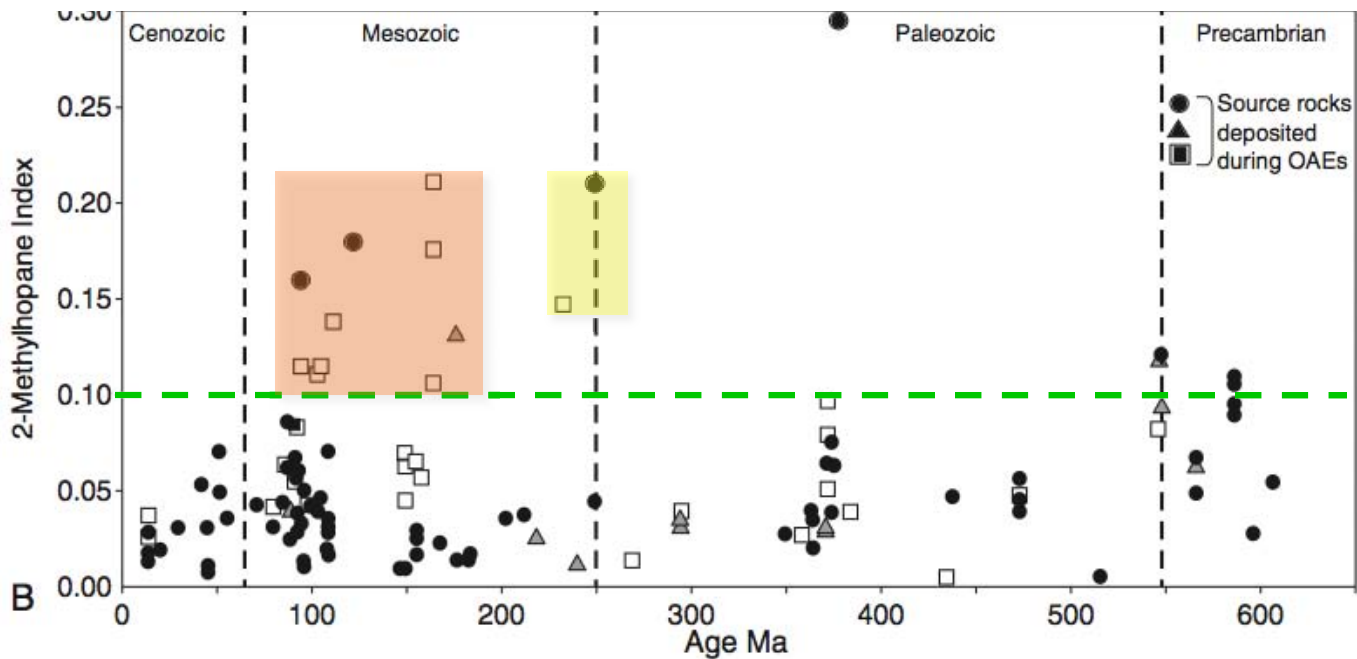
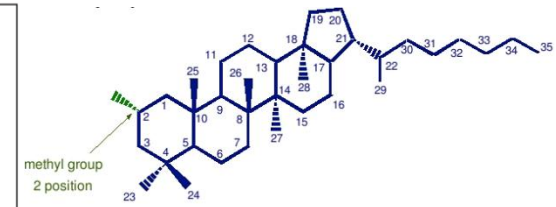
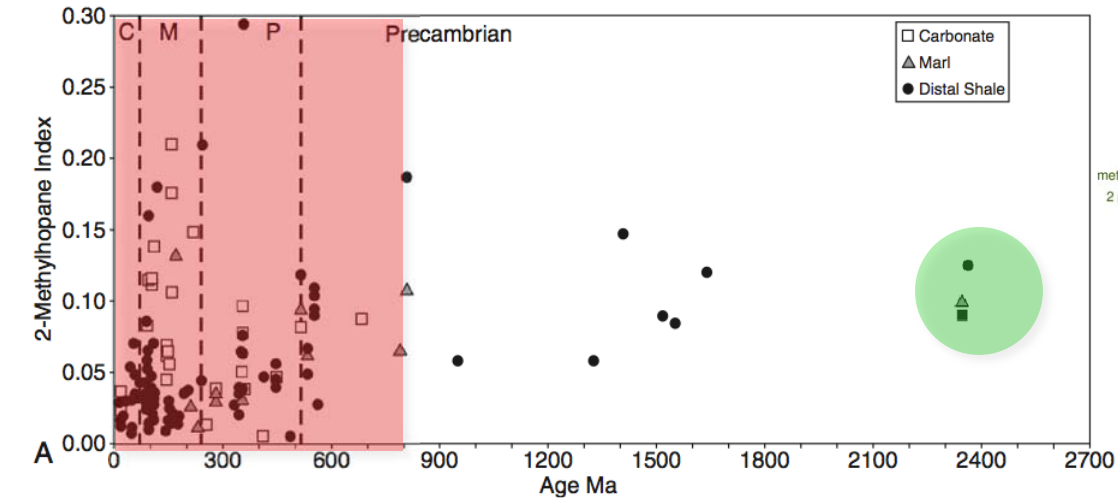
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# Biomarkers & phytoplankton evolution



After Knoll et al. (2007)

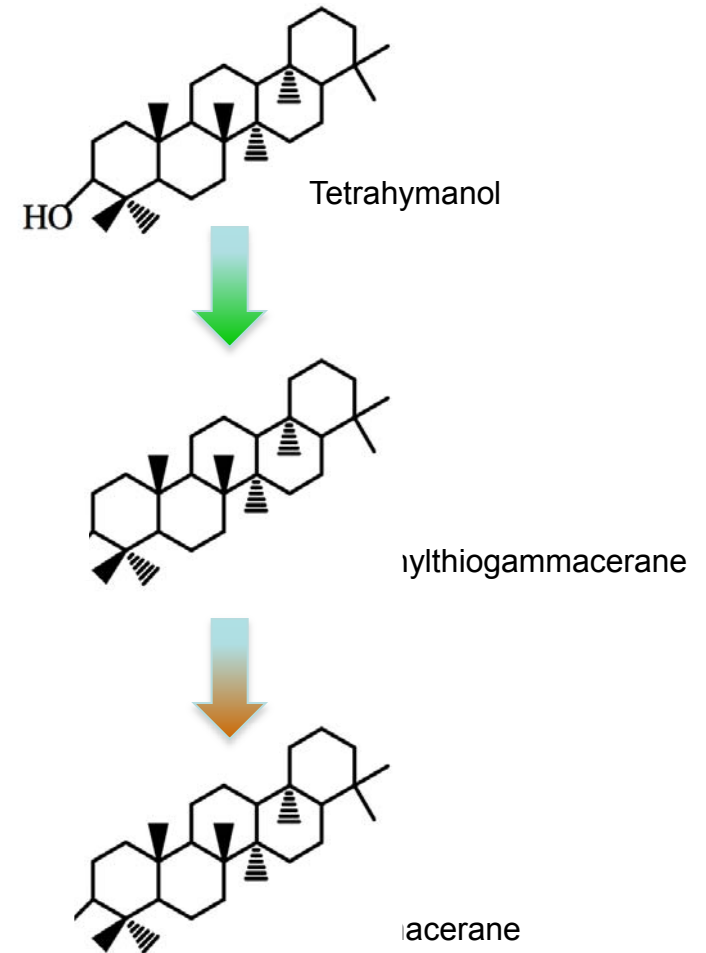
# Biomarkers for cyanobacteria



# **Proxies for water column stratification and oxygen deficiency**

# Tetrahymanol & Gammacerane

Miocene Gessoso-solfifera Formation



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# Lycopane

Mid-Cretaceous (Cenomanian-Turonian) OAE

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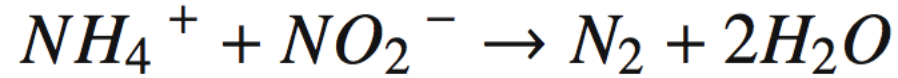
Surface sediments  
Arabian Sea

# Preservation of extended side-chain hopanes

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Köster *et al.* (1997, GCA)

# Anaerobic ammonium oxidation (anammox)



Lipids with linear concatenated cyclobutane moieties

[3]-ladderane 2-alkyl glycerol monoether

[5]-ladderane FAME

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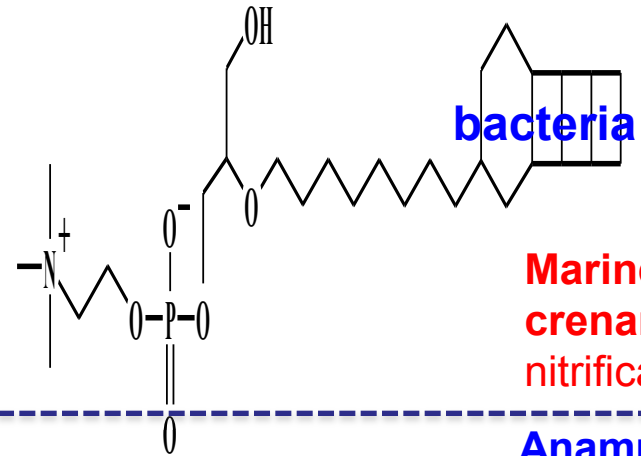
[3]-ladderane FAME

Sinninghe Damste et al. (2005, FEBS)

# Markers for nitrogen cycling

archaea

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Marine  
crenarchaea:  
nitrification

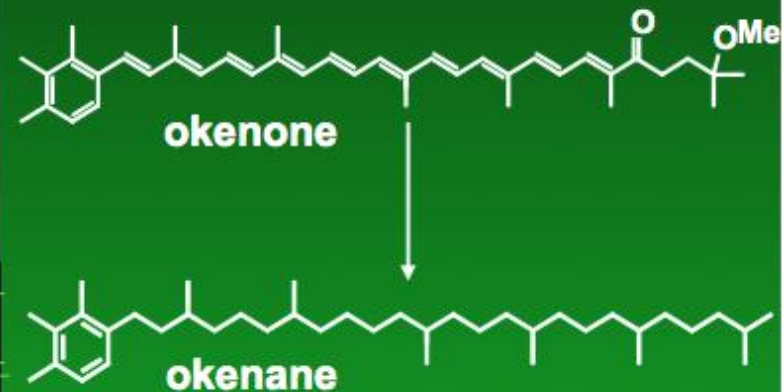
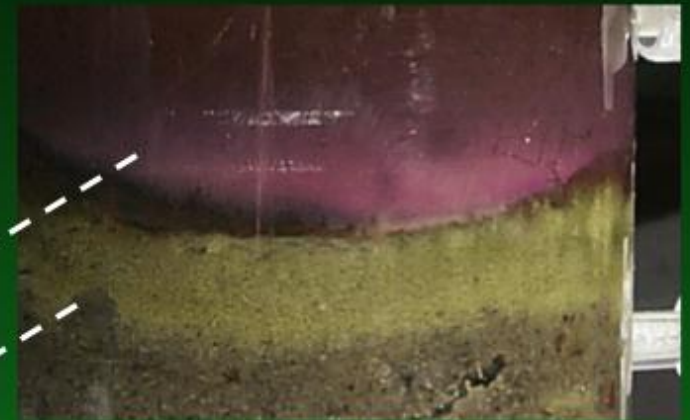
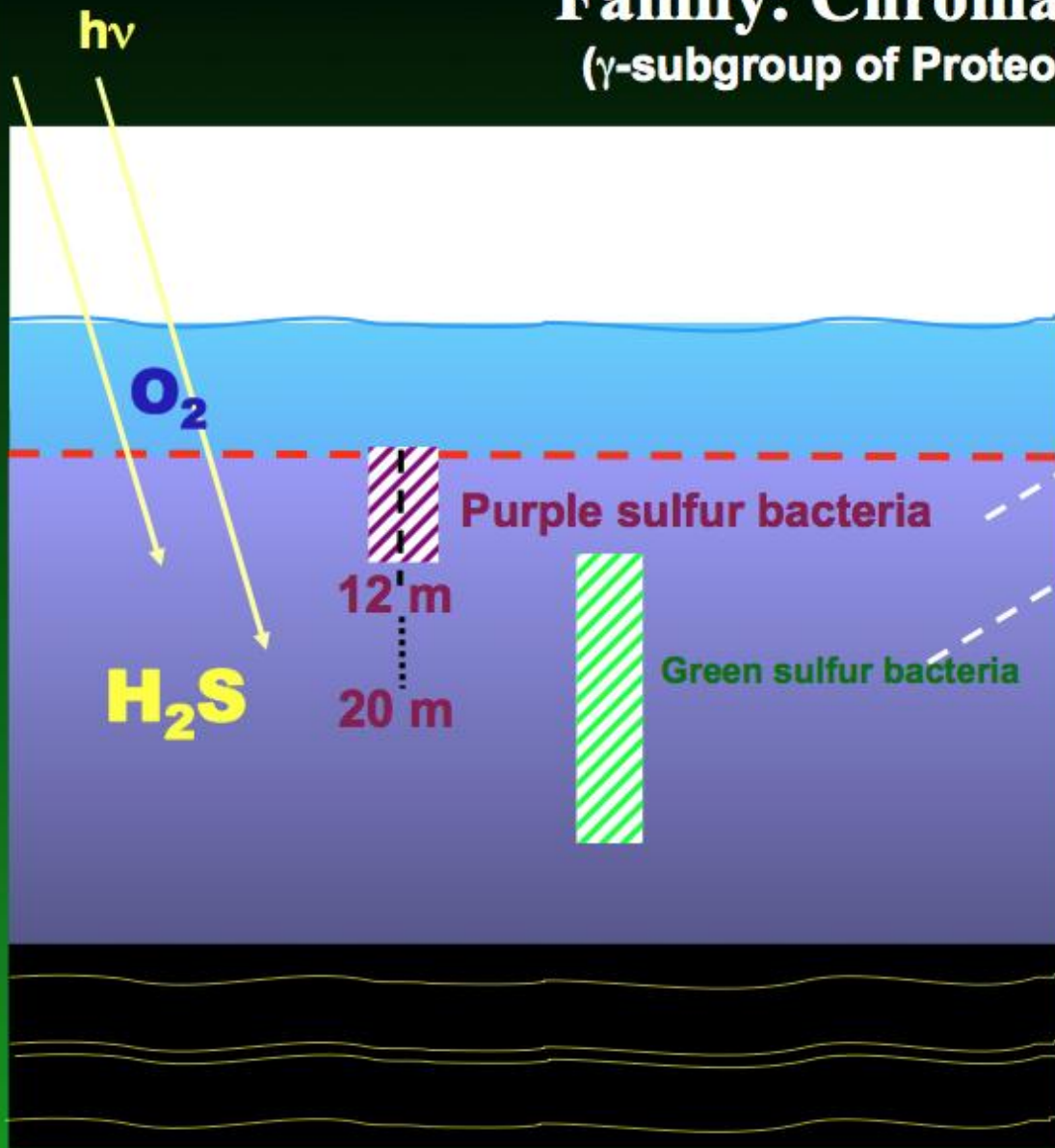
Anammox  
bacteria:  
Anaerobic  
oxidation of  
ammonium



# Purple sulfur bacteria

Family: Chromatiaceae

( $\gamma$ -subgroup of Proteobacteria)



Source: Roger Summons

# The Black Sea – water chemistry

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# The Black Sea - biomarkers

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# The Black Sea - biomarkers

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# The Black Sea - biomarkers

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# IPLs follow water column stratification: Black Sea

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Oxic: phototrophs

Suboxic: anoxygenic phototrophs  
Ammonium oxidizing crenarchaea

Anoxic: sulfate-reducing bacteria, unknown  
anaerobic bacteria

# BHPs in OMZs

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# BHPs in OMZs

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# Proxies for Sea Surface Temperature

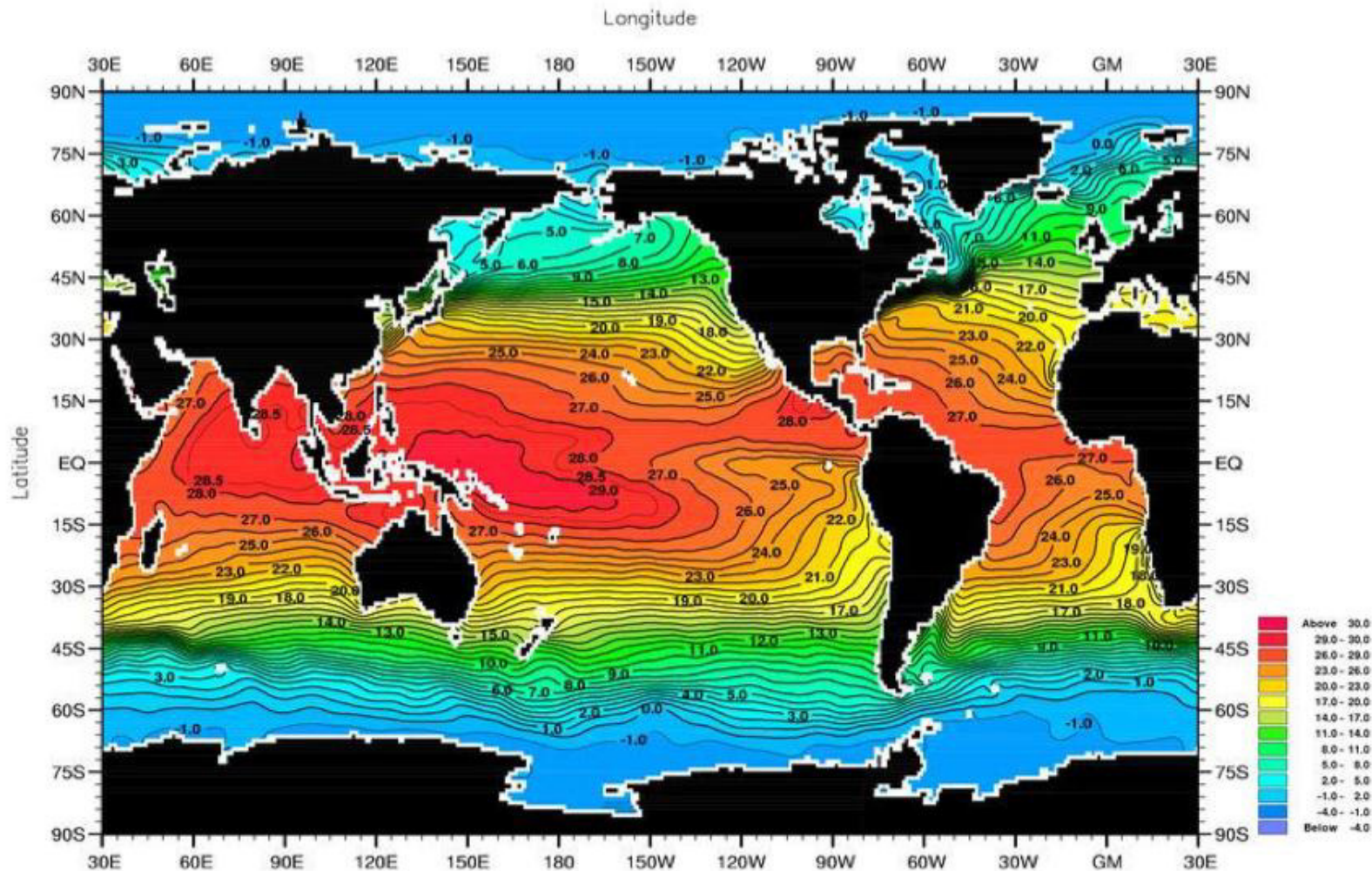


Fig. A2-1. Annual mean temperature ( $^{\circ}\text{C}$ ) at the surface.

Minimum Value= -1.93

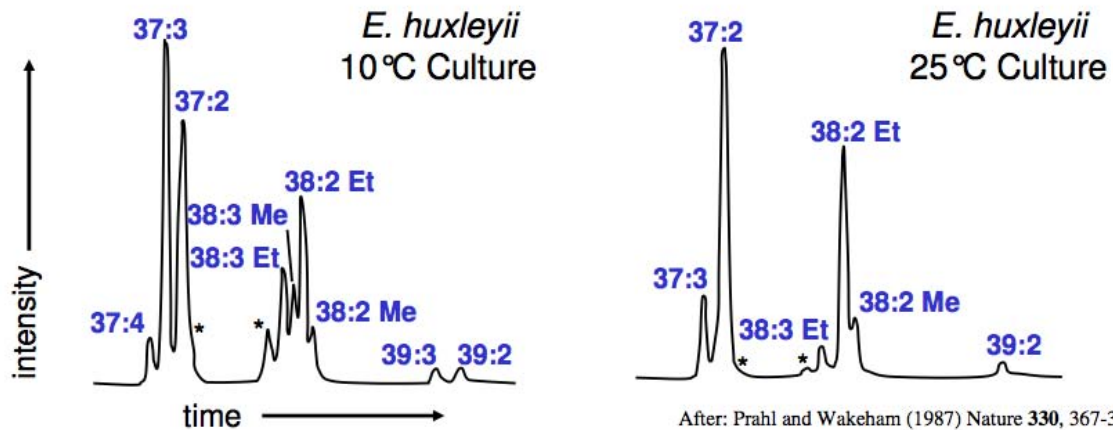
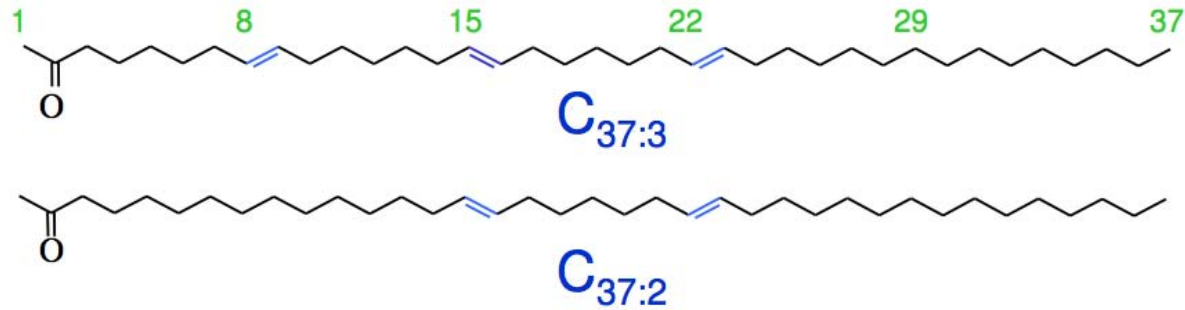
Maximum Value= 29.93

Contour Interval: 1.00

<http://www.nodc.noaa.gov>

Image courtesy of NOAA.

# Temperature proxies: Long-chain Alkenones



After: Prah and Wakeham (1987) Nature 330, 367-369

# Alkenones in marine surface sediments

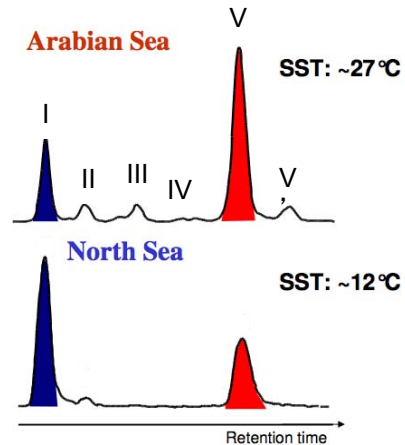
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# Sea Surface Temperature: TEX<sub>86</sub>

$$\text{TEX}_{86} = \frac{([\text{III}] + [\text{IV}] + [\text{V}'])}{([\text{II}] + [\text{III}] + [\text{IV}] + [\text{V}'])}$$

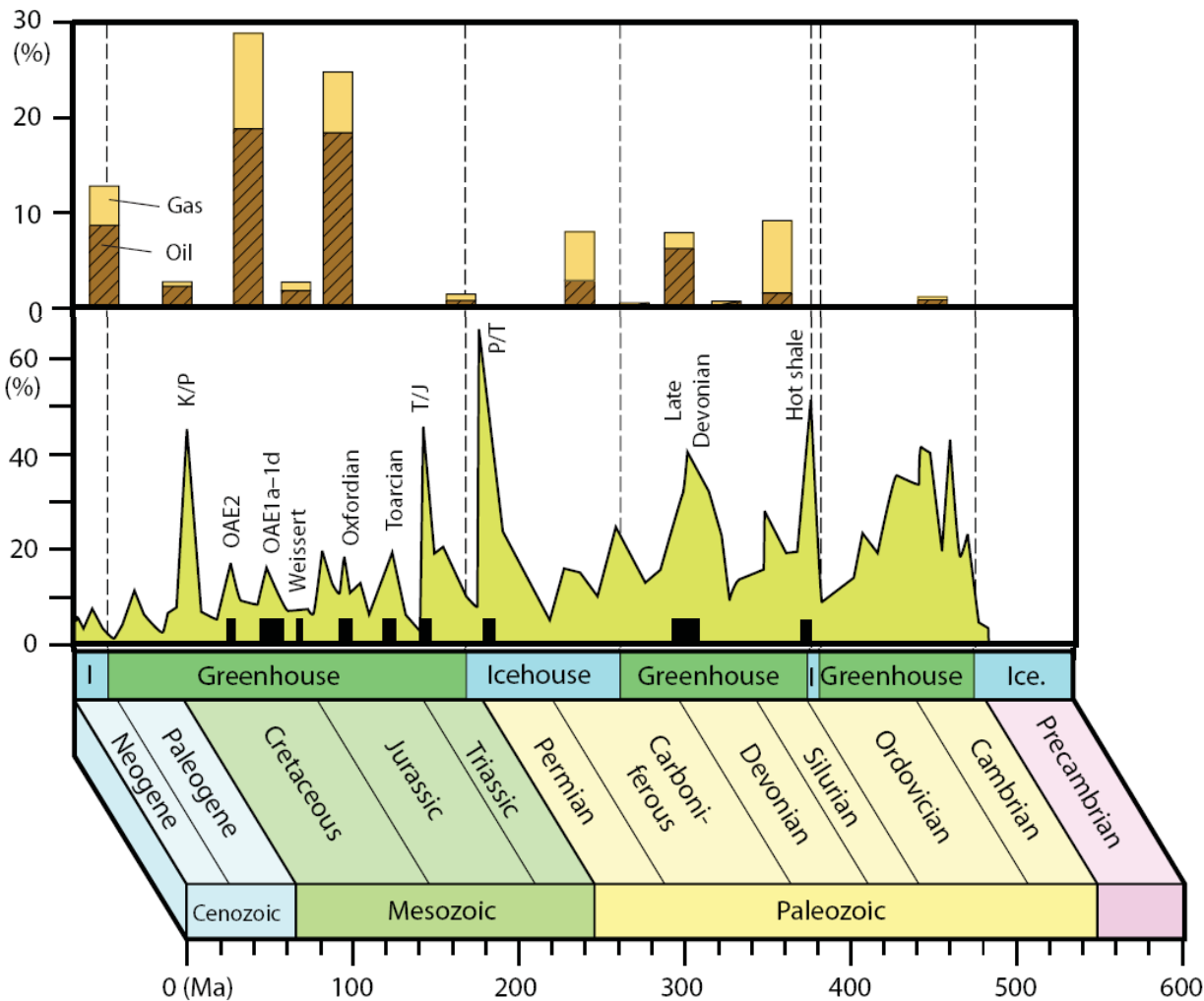
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# Oxygen deficiency in the past

# OAEs, extinctions & black shales

(G) Percent of world's original petroleum reserves generated by source rocks (Klemme and Ulminshek, 1991)



(F) Percentage extinction of marine genera (Raup and Sepkoski, 1986) and major Oceanic Anoxic Events

(G) Percent of world's original petroleum reserves generated by source rocks (Klemme and Ulminshek, 1991)

(F) Percentage extinction of marine genera (Raup and Sepkoski, 1986) and major Oceanic Anoxic Events

(E) Sea level changes and continental glaciation (Ridgwell, 2005)

(D) Temperature (Frakes et al., 1992)

(C) Carbon dioxide  
Ratio of the mass of atmospheric CO<sub>2</sub> at a past time to that at present (Berner, in press)

(B) Production rate of oceanic crust (Stanley, 1999)

(A) Climate mode (Frakes et al., 1992)

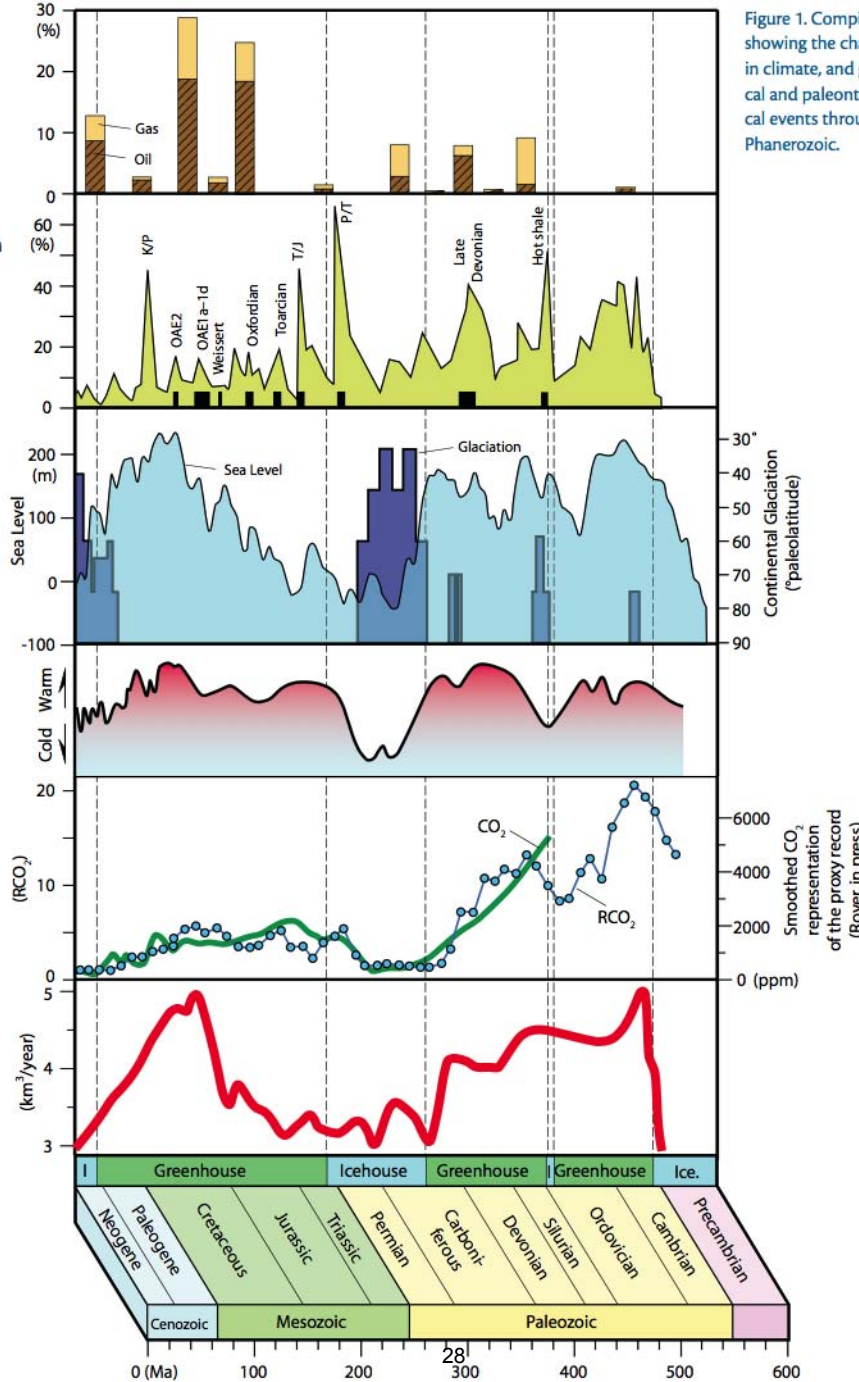


Figure 1. Compilation showing the changes in climate, and geological and paleontological events through the Phanerozoic.

# Ocean anoxia & black shale formation

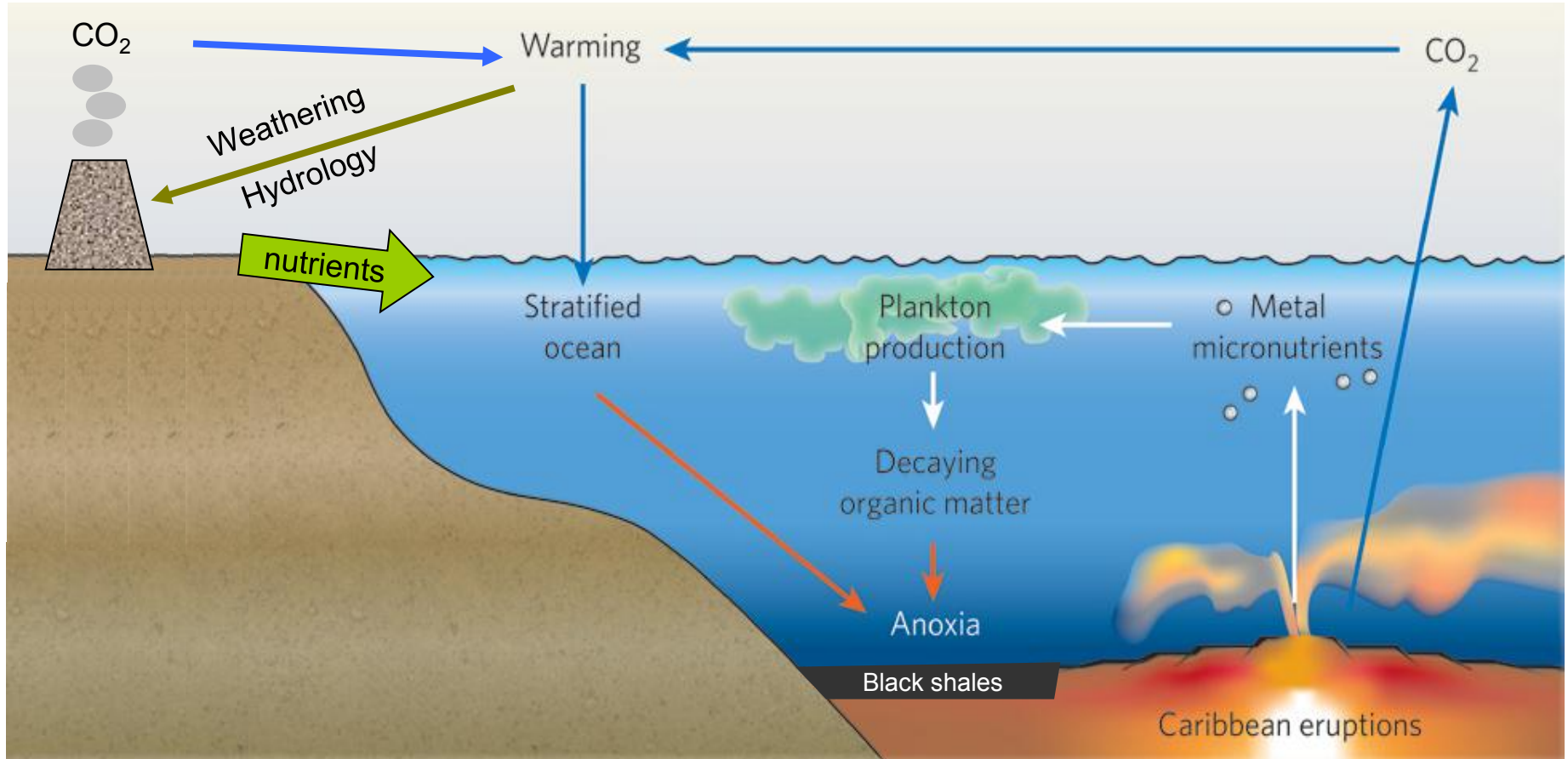
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Takashima *et al.* (2006, Oceanography)

# Feedback mechanisms & deoxygenation

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# Mechanisms for ocean anoxia: Volcanism



After Bralower (2008, Nature)  
Turgeon & Creaser (2008, Nature)  
Meyer & Kump (2008, Annu. Rev. Earth Planet. Sci)

# Mechanisms for ocean anoxia: Orbital forcing

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Zachos *et al.* (2001, Science)



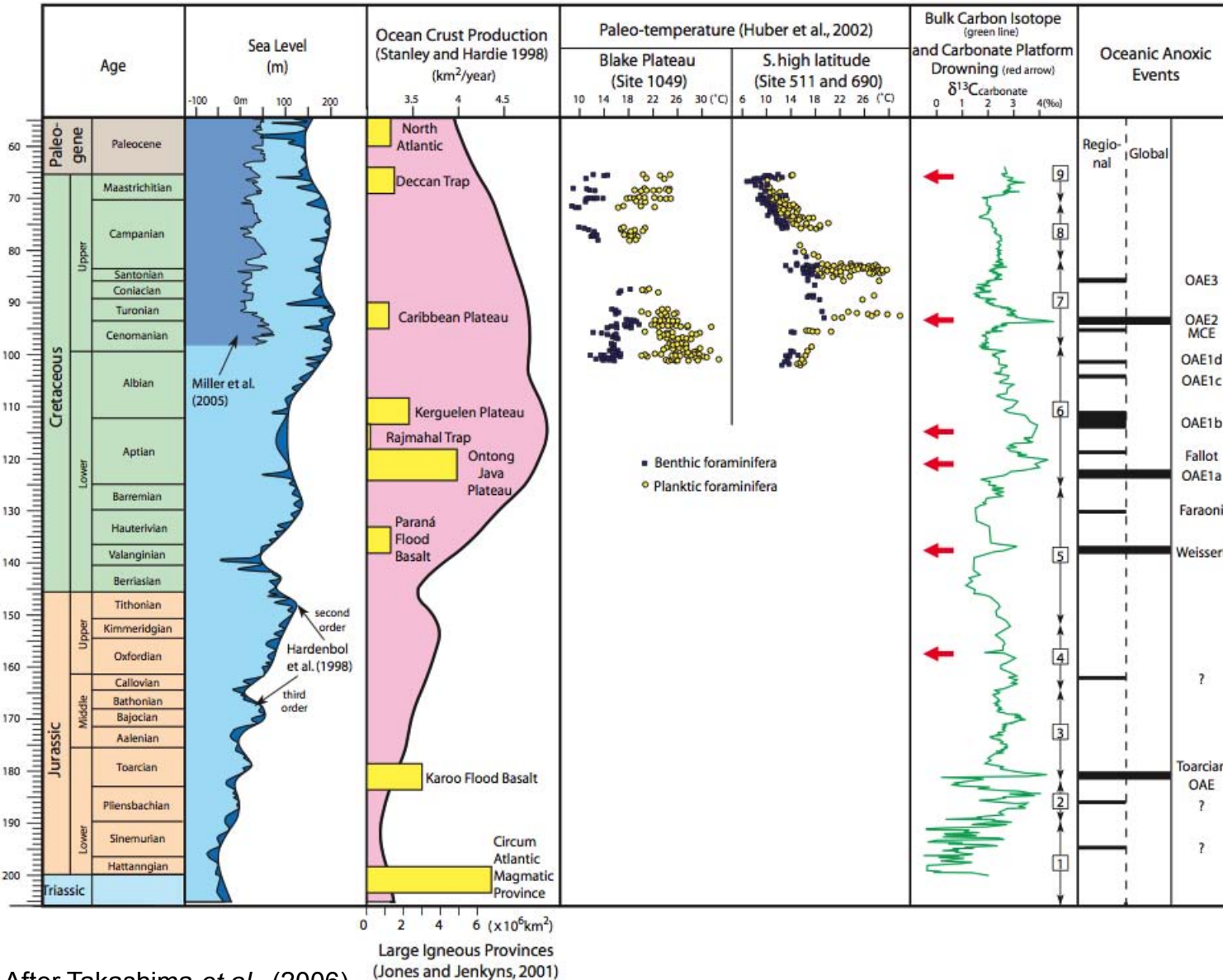
# **Oxygen deficiency in the past**

## **Cretaceous OAEs**

# The Cretaceous World & black shales

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# Oceanic Anoxic Events (OAEs)



Major perturbation in the global climate – ocean system

Chemical and/or biological changes in the world oceans

Black carbon-rich shales from deep oceans to sheaf seas

Enhanced productivity

Enhanced preservation of organic matter

Reduced circulation

# Small latitudinal temperature gradient

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- Intense volcanism & high  $p\text{CO}_2$
- Greenhouse climate & high sea surface temperatures
- Enhanced primary productivity
- Widespread anoxia and euxinia
- High burial of organic carbon
- Positive isotopic excursion

# Cenomanian-Turonian OAE-2

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# Large Igneous Provinces (IPLs) and OAEs

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# Cretaceous Sea Surface Temperatures

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# Cyanobacteria & N<sub>2</sub> fixation

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Kuypers *et al.* (2004 *Geology*)



# Cyanobacteria & N<sub>2</sub> fixation

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Kuypers *et al.* (2004 *Geology*)

# Massive expansion of Marine Archaea

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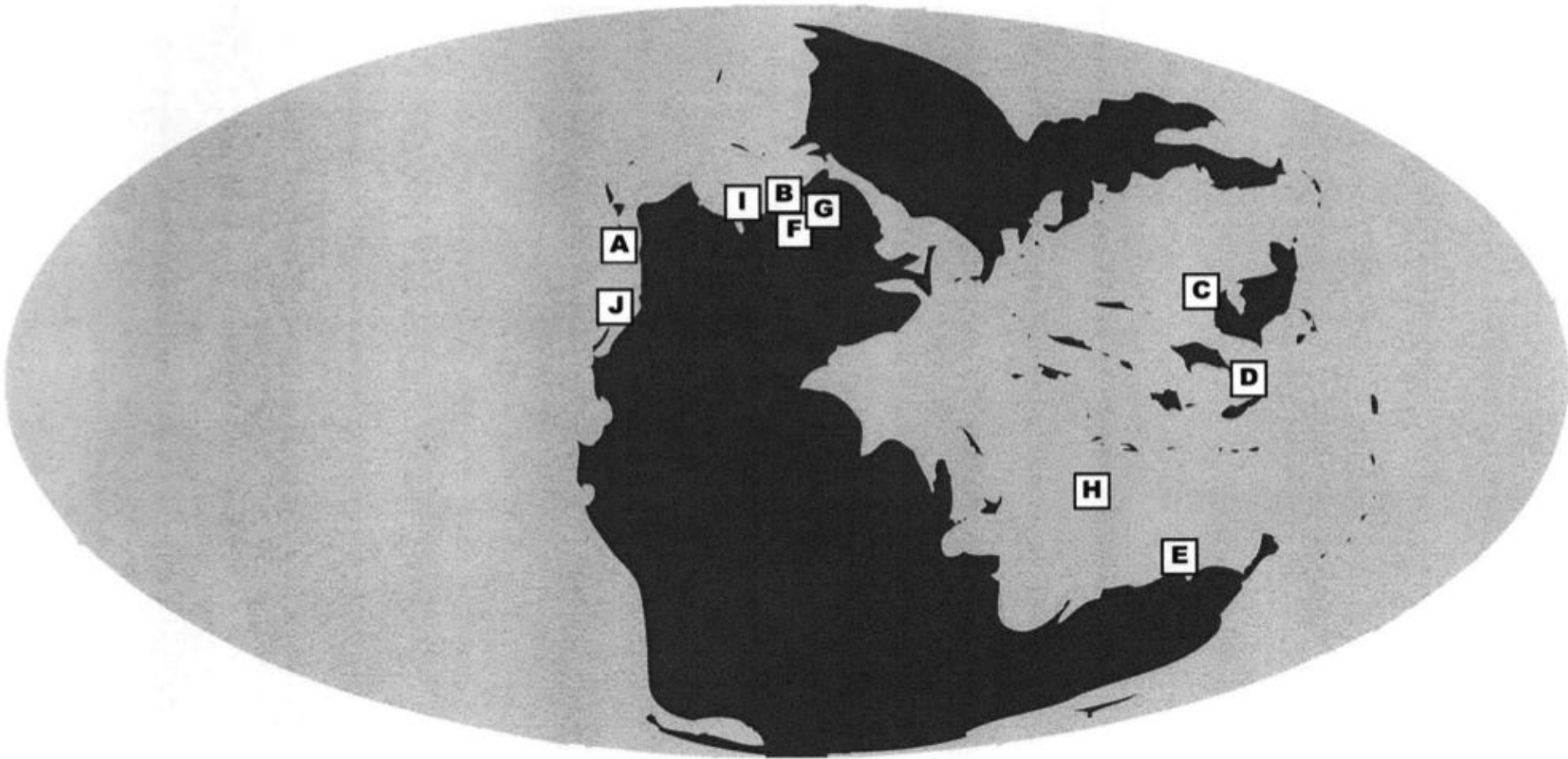
Kuypers *et al.* (2001)

# **Oxygen deficiency in the past Permian-Triassic boundary**

# Permian-Triassic mass extinction (~252 Ma)

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# Photic zone euxinia at the P-T



**Figure 7.4 Global map from the Permian-Triassic boundary.** Chlorobi-derived biomarkers have been identified in the sites noted. (a) Peace River, Canada. (b) Kap Stosch, Greenland. (c) Meishan, China. (d) Great Bank of Guizhou, China. (e) Perth Basin, Australia. (f) Kupferschiefer Basin, Germany. (g) Spitsbergen, Norway. (h) Tibet. (i) Blind Fiord, Canada. (j) Opal Creek, Canada. Map modified from Scotese Paleomap Project website.

Image courtesy<sup>46</sup> of MIT Press.

# Meishan, southern China

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# Nitrogen fixation across the P-T

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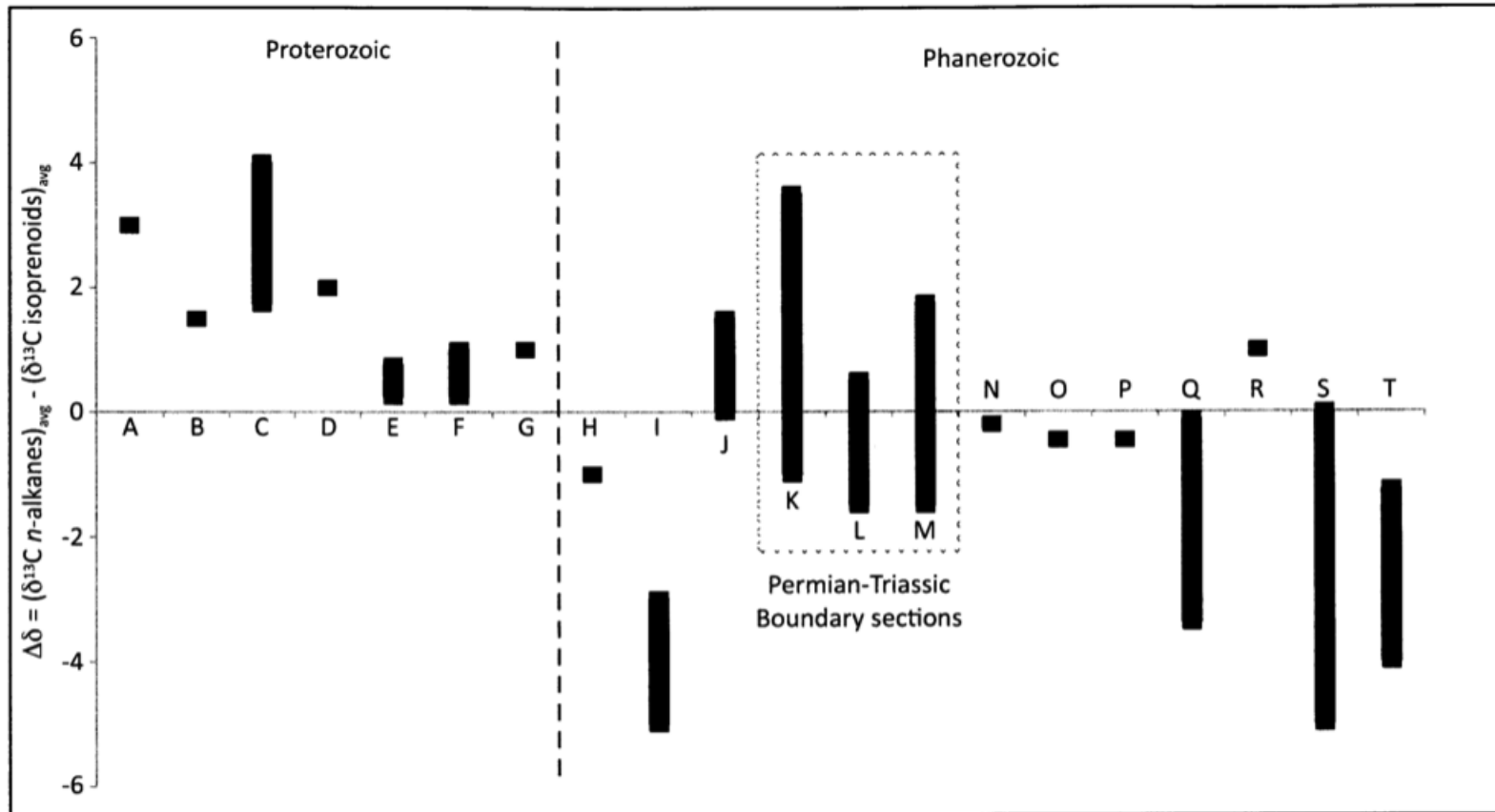
# Western Australia

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# Isotope anomaly

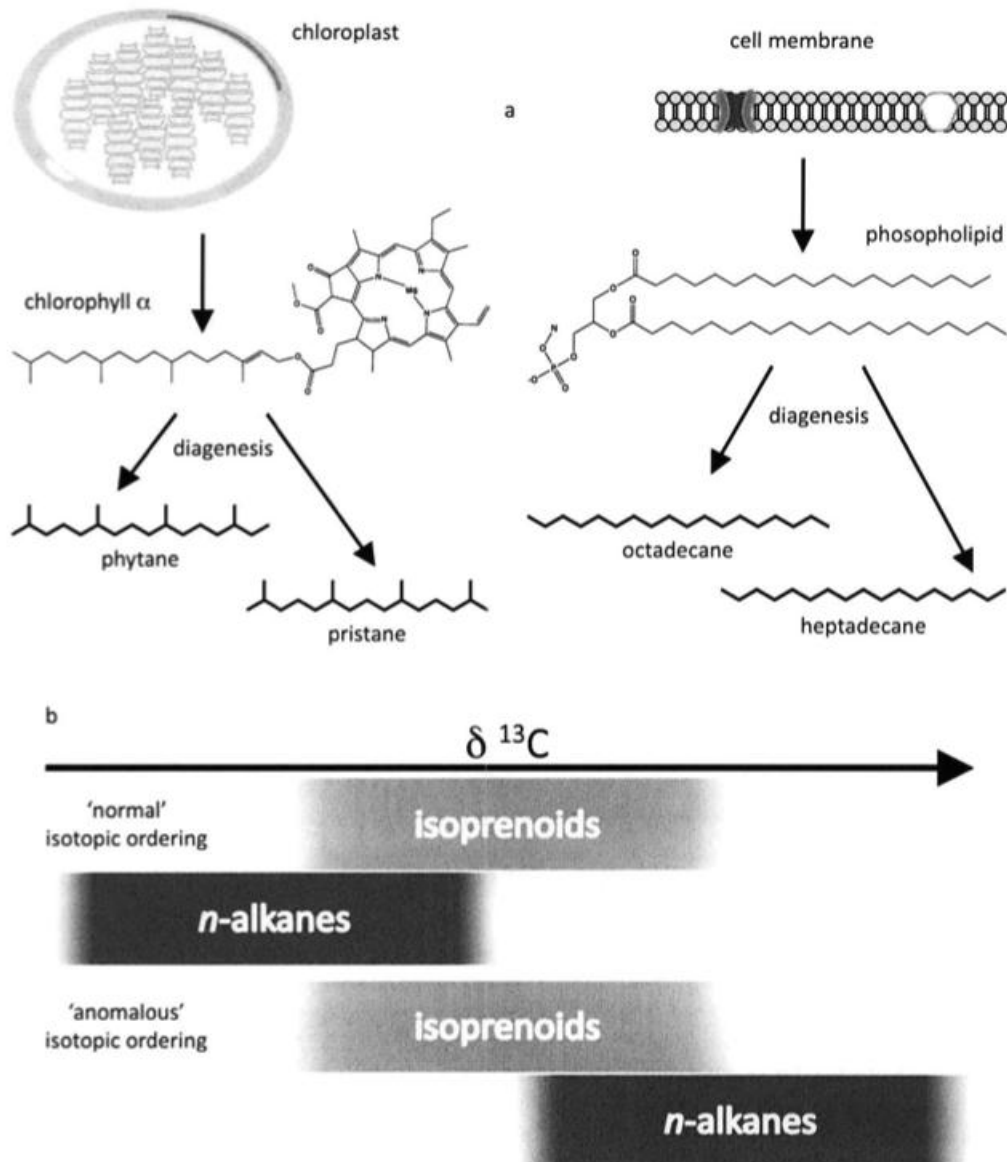
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# Isotope anomaly



**Figure 1.5 Enrichment of *n*-alkanes relative to isoprenoids from a range of environments.** K, from Meishan, China and L, from Peace River Basin, Canada, were measurements made in this thesis from the Permian-Triassic boundary; M, from the Perth Basin, Australia (Grice et al. 2005) is also from this boundary. J and R are from Phanerozoic basins deposited beneath anoxic water columns. A Mount Bruce Supergroup, Pilbara Craton, Australia, 2.78-2.45Ga (Brocks et al. 2003). B Barney Creek Formation, McArthur Basin, Australia, 1690Ma; C Nonesuch Formation, USA, 1055Ma; D Walcott Member, Chuar Group, USA, 850Ma; E Bitter Springs Formation, Amadeus Basin, Australia, 800Ma; F Visingso Group, Sweden, 775Ma (Logan et al. 1995). G South Oman Salt Basin, Buah Formation, Oman, 600Ma; H South Oman Salt Basin, Buah Formation, Oman, 547Ma (Kelly 2009). I Officer Basin, Australia, 510Ma; J Maquoketa Group, Illinois Basin, USA, 450Ma (Logan et al. 1995). N Paris Basin Shale, France, 180Ma; O West Hammersfest Basin, Barents Sea, 168Ma; P Guatamalan Carbonate, 100Ma (Bjoroy 1992). Q Eastern Llanos Basin, Colombia, 65Ma (Cortez et al 2010). R Green River Shale, USA, 40Ma; S Baise Basin, Guanxi, China and Mulhouse Basin, Alsace, France, 28Ma (Logan et al. 1995). T Modern cultured algal lipids (Schouten et al. 1998).

# Isotope anomaly



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